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Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor

Sheng Chang, Zengli Zhao *, Anqing Zheng, Xiaoming Li, Xiaobo Wang, Zhen Huang, Fang He, Haibin Li

Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Science, Guangzhou 510640, People's Republic of China

HIGHLIGHTS

- Pretreated eucalyptus wood gave higher bio-oil yield than original eucalyptus wood.
- Contents of ketones and acids in bio-oil were lowered by hydrothermal pretreatment.
- Hydrothermal pretreatment significantly enhanced levoglucosan content in bio-oil.
- Hydrothermal pretreatment improved fuel quality of bio-oil.

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ABSTRACT

Eucalyptus wood powder was first subjected to hydrothermal pretreatment in a high-pressure reactor at 160–190 °C, and subsequently fast pyrolyzed in a fluidized bed reactor at 500 °C to obtain high quality bio-oil. This study focused on investigating effect of hydrothermal pretreatment on bio-oil properties. Hemicellulose and some metals were effectively removed from eucalyptus wood, while cellulose content was enhanced. No significant charring and carbonization of constituents was observed during hydrothermal pretreatment. Thus pretreated eucalyptus wood gave higher bio-oil yield than original eucalyptus wood. Chemical composition of bio-oil was examined by GC/MS and ^{13}C NMR analyses. Bio-oil produced from pretreated eucalyptus wood exhibited lower contents of ketones and acids, while much higher levoglucosan content than bio-oil produced from original eucalyptus wood, which would help to improve thermal stability of bio-oil and extract levoglucosan from bio-oil. Hydrothermal pretreatment also improved bio-oil fuel quality through lowering water content and enhancing heating value.

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1. Introduction

The growing concern with depletion of fossil fuels and global climate change provides impetus to the use of renewable biomass resources, and great efforts are placed on the production of chemicals and liquid fuels from biomass through a variety of possible conversion approaches (McKendry, 2002; Maniatis and Millich, 1998). Fast pyrolysis as a thermochemical procedure has become a candidate pathway for producing chemicals and fuels from biomass. By this process up to 70–80% of the dry biomass can be directly converted into a liquid fuel called bio-oil that is readily stored and transported (Bridgwater and Peacocke, 2000; Uzun et al., 2006). In general, this process is conducted in the absence of oxygen at the carefully controlled temperature of around 500 °C with very high heating rates (>100 °C/s), short hot vapours residence times inside the reactor (typically less than 2 s) and rapid cooling of vapour (Bridgwater, 2012). The resulting bio-oil is a dark brown liquid that can be taken as a supplement for conventional petroleum oils. However, the chemical composition of biomass-derived oil is quite different from that of petroleum-derived oils. High contents of water and oxygenated organic compounds in bio-oil are mainly responsible for the poor fuel quality of bio-oil (Oasmaa and Czernik, 1999). The complexity of chemical composition makes fractional distillation of bio-oil to extract high added-value chemicals difficult (Mohan et al., 2006). Interaction of lightweight reactive compounds in bio-oil to form larger molecular results in the thermal unstability and phase separation of bio-oil during storage and transportation (Diebold and Czernik, 1997). Moreover, the significant corrosion of thermal devices during the application of bio-oil may be caused by the organic acids in bio-oil. Therefore, the quality improvement of bio-oil will be desired for more effective application.

Most compounds in bio-oil are essentially derived from the depolymerization of hemicellulose, cellulose and lignin in biomass during fast pyrolysis, and the physical and chemical properties of bio-oil are obviously feedstock dependent. Thus pretreatment to modify the chemical composition of biomass will affect the bio-oil properties. Recently, biomass torrefaction as a thermal

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* Corresponding author. Tel.: +86 02087057721; fax: +86 02087057737.
E-mail address: zhaozl@ms.giec.ac.cn (Z. Zhao).

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pretreatment for fast pyrolysis has received an increasing interest (Liawa et al., 2013; Meng et al., 2012). Torrefaction is also called as mild pyrolysis and conducted in the temperatures range of 200–300 °C (Chen et al., 2011). By this process, most of hemicellulose in biomass can be removed from biomass, and plenty of water and some lightweight organic compounds consisting of ketones, aldehydes, alcohols, and acids are produced from degradation of main constitutes in biomass (Prins et al., 2006; Wannapeera et al., 2011). Consequently, water and other lightweight compounds are less formed in the subsequent fast pyrolysis of torrefied biomass with less hemicellulose. Thus more stable bio-oil with lower water content is obtained from fast pyrolysis of torrefied biomass. The torrefaction-aid fast pyrolysis is considered as a step-wise pyrolysis, in which major biomass constituents with different thermal stability are desired to be selectively converted into target products with less complexity. The main purpose of torrefaction treatment prior to fast pyrolysis is to degrade selectively hemicellulose in biomass. However, the charring and cross-linking of other biomass constituents occur during torrefaction. Thus the selective pyrolysis for major chemical components can not be achieved effectively. Bio-oil yields in fast pyrolysis of torrefied biomass are significantly reduced with torrefaction severity owing to detrimental effect of torrefaction on chemical structure of biomass constituents, although obvious quality improvement of bio-oil can be achieved by torrefaction treatment (Zheng et al., 2012, 2013). Seeking more effective pretreatment methods for removing hemicellulose from biomass is desired to obtain higher quality bio-oil with less yield penalties.

Hydrothermal pretreatment which is also referred to as wet torrefaction is an effective method for fractionating biomass in hot compressed liquid water (Allen et al., 1996). The process generally is carried out under the saturated vapor pressure at temperatures varying from 150 to 260 °C. During hydrothermal pretreatment, hemicellulose in biomass can be completely solubilized into aqueous compounds, the lignin seal is broken, and cellulose is almost entirely preserved in the solid product (Laser et al., 2002; Sasaki et al., 2002). The process significantly increases the accessibility of cellulose to enzyme and is mainly used as a pretreatment method for subsequent enzymatic hydrolysis of cellulose. In view of effective removal of reactive hemicellulose from biomass, hydrothermal pretreatment will also be a potential pretreatment method prior to fast pyrolysis to improve quality of bio-oil through decreasing the formation of water, acids, and other reactive compounds in fast pyrolysis. Particularly, severe charring and cross-linking of biomass constitutes may be avoided in hydrothermal pretreatment owing to relatively mild reaction condition, which will help to reduce bio-oil yield penalties in fast pyrolysis. In addition, the ash may be removed from biomass during hydrothermal pretreatment, which will be also helpful to fast pyrolysis. However, hydrothermal pretreatment as a pretreatment method for fast pyrolysis has been less considered in previous literatures.

Eucalyptus is one of most important fast-growing trees, and approximately 3.5 million hectares of eucalyptus plantation with the productivities of 15–30 m^3/ha/a have been established in South China (Zhou and Wingfield, 2011). Currently, eucalyptus is mainly utilized for pulp production and furniture making, where plenty of wood residue is produced and has not been utilized effectively. Therefore, eucalyptus wood was selected as biomass feedstock in the present study. The samples were first subjected to hydrothermal pretreatment in a high-pressure batch reactor in the temperature range of 160–190 °C for 5 min. Subsequently, the fast pyrolysis of pretreated eucalyptus wood was conducted in a fluidized bed reactor to acquired higher quality bio-oil. The main aim was to investigate the effects of hydrothermal pretreatment on physical and chemical properties of bio-oil.

Table 1
Mass yield and chemical component analysis of pretreated eucalyptus wood (on dry basis).

Samples	Mass yield (wt%)	Chemical component[a] (wt%)		
		Hemicellulose	Cellulose	Acid insoluble fibers
Eucalyptus wood		24.02	44.08	28.25
PE-160	96.45	21.85 (87.75)	45.28 (99.07)	27.74 (94.69)
PE-170	90.82	18.02 (68.14)	47.90 (98.68)	28.07 (90.23)
PE-180	81.51	8.82 (29.93)	50.39 (93.16)	30.60 (88.27)
PE-190	73.29	3.47 (10.58)	52.59 (87.44)	31.86 (82.65)

[a] Values in the parentheses are the recovery rate of chemical components in pretreated eucalyptus wood.

2. Methods

2.1. Material preparation

Eucalyptus wood used in this study was acquired from a local wood processing factory in Guangzhou, China. Prior to hydrothermal pretreatment, the samples were ground to small particle size and subsequently sieved to a mean particle size of 0.25–0.42 mm. Then these selected particles were oven-dried to around 6% moisture content. The results of chemical component analysis of the samples were listed in Table 1.

2.2. Hydrothermal pretreatment of eucalyptus wood

Hydrothermal pretreatment of eucalyptus wood was carried out in a high-pressure batch reactor at 160, 170, 180, and 190 °C for 5 min. Severe degradation of cellulose in eucalyptus wood could be avoided at such relatively low temperatures and short retention

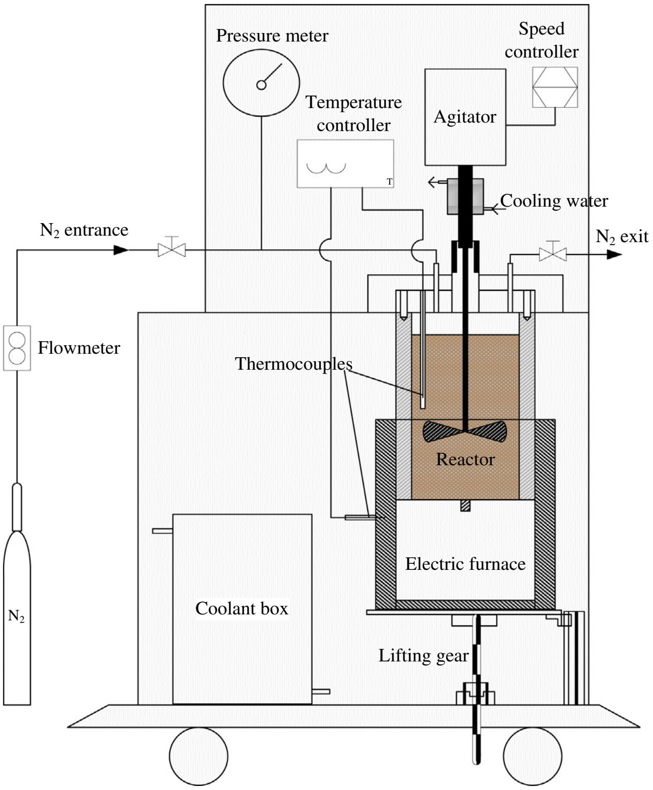

Fig. 1. Schematic diagram of the high-pressure batch reactor for hydrothermal pretreatment.

time. This apparatus was formed by a stainless steel pressure vessel (reactor), electric furnace for heating the reactor, temperature controller, agitator for mixing the samples, coolant box for cooling the reactor, and lifting gear for raising the height of electric furnace and coolant box (Fig. 1). A mixture of eucalyptus wood and water (1:9, w/w) was put into the reactor. The oxygen in the reactor was eliminated using the nitrogen gas flow of 1 L/min for 20 min. Then the reactor with magnetic agitator operating at 600 rpm was heated up to desired temperatures within 10–15 min using the electric furnace. After maintaining the reaction temperature for 5 min, the reactor was cooled quickly to <100 °C to terminate the reaction using the coolant box with cooling water circulation. The pretreated eucalyptus wood was obtained by filtrating the reaction product, and washed carefully with water for several times. Then the pretreated eucalyptus wood was oven-dried at 105 °C for about 15 h to the moisture content of 5–6%. The mass yield was calculated as the dry weight of original eucalyptus wood divided by the dry weight of pretreated eucalyptus wood. Six parallel experiments were performed for each reaction temperature, and experimental results were found to be highly reproducible.

2.3. Characterization of pretreated eucalyptus wood

The content of hemicellulose, cellulose, and acid insoluble fibers in pretreated eucalyptus wood was analyzed using the method developed by Van Soest (Goering and Van Soest, 1970). The sample of 0.5–1.0 g was treated in a neutral-detergent solution that was prepared by dissolving 30 g sodium lauryl sulfate, USP; 18.61 g disodium ethylenediaminetetraacetate (EDTA), dihydrate crystal; 6.18 g sodium borate decahydrate; 4.56 g disodium hydrogen phosphate, anhydrous, and 10 ml 2-ethoxyethanol in 1 L distilled water. The insoluble fibers were defined as NDF (hemicellulose, cellulose, and lignin). Then the sample of 0.5–1.0 g was treated in an acid–detergent solution that was prepared by dissolving 20 g cetyl trimethylammonium bromide (CTAB) in 1 L sulfuric acid of 0.5 mol/L. After digestion, the hemicellulose was solubilized, and the insoluble fibers were defined as ADF (cellulose and lignin). Thus content of hemicellulose could be calculated by subtracting NDF content with ADF content. The obtained NDF was further digested with 72% sulfuric acid. After digestion, cellulose was decomposed and filtered away. The final residues exclusive of ash were expressed as acid insoluble fibers (mostly lignin). The content of cellulose could be calculated by subtracting ADF content with the content of acid insoluble fibers. All analyses were performed in duplicate, and the results were averaged to report the content of chemical components in samples. To investigate the degree of decomposition of chemical components in eucalyptus wood during hydrothermal pretreatment, recovery rate of chemical components in pretreated eucalyptus wood was defined as follow:

$$\text{Recovery rate }(\%) = \frac{\begin{array}{c}\text{Chemical component content}\\ \text{in pretreated eucalyptus wood}\end{array}}{\begin{array}{c}\text{Chemical component content}\\ \text{in original eucalyptus wood}\end{array}} \times \text{Preatreated eucalyptus wood yield}$$

The metal analysis of pretreated eucalyptus wood was performed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 8000, PerkinElmer, U.S.A.). The sample of about 0.15 g was digested for about 6 h in the 4 ml mixed acids of concentrated HNO_3 and $HClO_4$ (3:1, v/v). The digested sample was diluted to 10 ml with distilled-deionized water. In ICP-OES analysis, the gold wavelength with the highest sensitivity was used. Main operating conditions included nebulizer flow of 1.5 L/min, sample introduction flow of 1.5 ml/min, flush time of 10 s, delay time of 40 s, and wash time of 40 s. Five standard solutions of each metal were prepared and analyzed to generate external calibration curves for quantitative determination. Each sample was test in triplicate for quality assurance.

2.4. Fast pyrolysis experiments of pretreated eucalyptus wood

Fast pyrolysis experiments of pretreated eucalyptus wood were conducted in a 1 kg/h bench-scale fluidized bed reactor system.

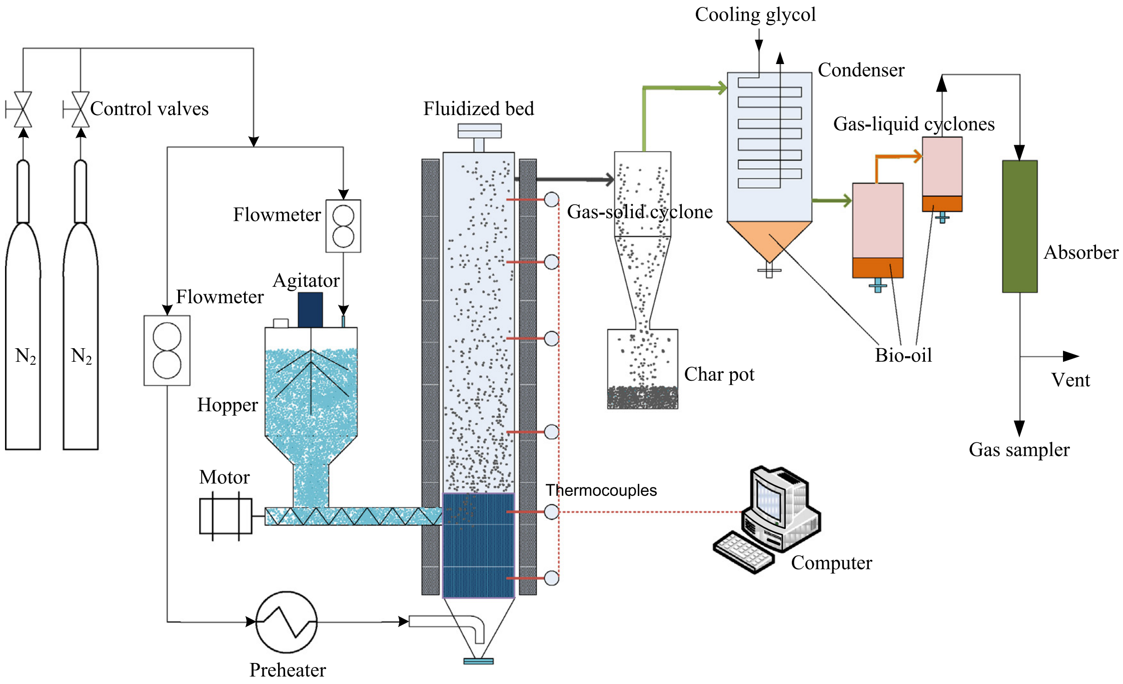

Fig. 2. Schematic diagram of the fluidized bed reactor for fast pyrolysis.

The schematic drawing of this system was depicted in Fig. 2. It was mainly composed of a screw feeder, a gas preheater, a fluidized bed reactor, a gas–solid cyclone, a coil pipe condenser, two gas–liquid cyclones, and an absorber with cotton. The fluidized bed reactor was made of a stainless steel with an internal diameter of 7.6 cm and a height of 90 cm. The inert silica sand of around 1 kg with mean diameter of 0.18–0.25 mm was put into the reactor as heat transfer medium. The reactor was heated using electric heating jackets and was temperature controlled by computer. A nitrogen gas flow of 50 L min^{-1} was used as a carrier gas to fluidize the sand bed. Eucalyptus wood samples were stored in a hopper. After the stable reactor temperature condition of 500 °C was established, the samples were continuously fed by the screw feeder at a rate of about 1 kg/h into the reactor. The sample particles were heated by hot fluidized medium and the thermal decomposition of particles occurred once reaching the inside of reactor. Pyrolysis vapour consisting of condensable components, permanent gas and pyrolysis char were produced in the reactor. The product mixture was quickly carried out of the reactor by the nitrogen gas and the pyrolysis char particles were separated from the mixture by the gas–solid cyclone and collected in the char pot. Subsequently, pyrolysis vapour entered into the coil pipe condenser with circulating cooling glycol maintained at about −10 °C and was cooled rapidly. Part of pyrolysis vapour was condensed in the condenser, and other liquid components were sequentially separated from permanent gas by two gas–liquid cyclones assembled in series. The liquid product obtained as bio-oil was the mixture of the liquid collected in condenser and the liquid collected by gas–liquid cyclones. Permanent gas was sampled and vented after passing the absorber. The amount of bio-oil and char produced was recorded by gravimetric analysis. Each experiment was repeated twice under the same conditions to ensure the reproducibility of results. The yield of three-phase products was defined as follows:

$$\text{Yield of bio}-\text{oil}\ (\%) = \frac{\text{Weight of bio}-\text{oil}}{\text{Dry weight of pretreated eucalyptus wood}} \times 100\%$$

$$\text{Yield of char}\ (\%) = \frac{\text{Weight of char}}{\text{Dry weight of pretreated eucalyptus wood}} \times 100\%$$

$$\text{Yield of gas}\ (\%) = 100 - \text{yield of bio-oil} - \text{yield of char}$$

2.5. Characterization of bio-oil

Gas chromatography mass spectroscopy (GC/MS) analysis of bio-oil was performed on a gas chromatograph (7890A, Agilent Technologies, U.S.A.) coupled with a mass spectrometer (5975C, Agilent Technologies, U.S.A.). A HP-INNOwax capillary column (Agilent 19091N-133, Polyethylene Glycol, 30 m × 0.25 mm, 0.25 μm film thickness) with a carrier gas flow velocity 36.4 cm/s was used for the chromatographic separation of chemical components in bio-oil. About 200 mg bio-oil was dissolved in 10 ml GC-grade acetone, and sample size of 1 μL was used in GC analysis. The injector temperature was 240 °C, and a split ratio 20:1 was used. The GC oven temperature program was 2 min at 50 °C, 10 °C/min to 90 °C, 4 °C/min to 120 °C, and then 8 °C/min to 230 °C with a dwell time of 29 min. The mass spectrometer was operated in electron impact mode at 70 eV. After a solvent delay of 2.8 min, full scan mass spectra were acquired from 12 to 500 m/z. The identification of the main peaks was made from NIST11 MS library and previously published literatures. Some standard compounds corresponding to the proposed assignments for the peaks in the initial GC/MS analysis were used to confirm the peak identification based on matching the retention time and mass spectrum. The standard compounds used were purchased from Sigma–Aldrich. They were further used to calibrate the GC column. The five standard solutions of each of these pure compounds with the concentrations of 400, 800, 1200, 2000, and 4000 μg/ml were prepared by dissolving them in acetone. Then GC analyses of standard solutions with sample size of 1 μL were conducted, and the peak area of each calibration compound was obtained. To establish the calibration curve for each standard compound, the peak area of the compound was plotted against the mass of the compound in the 1 μL solution and then linearly regressed (with R^2 value $\geqslant 0.98$). The mass of the compounds in bio-oil which were not calibrated was estimated by the calibration curves of standard compounds with the nearest retention time on the GC column or the similar chemical structure. Thus the content of detected compounds in bio-oil could be calculated as the mass of bio-oil used in GC analysis divided by mass of compounds. Two parallel analyses were performed for each bio-oil sample, and the content of compounds was the average of two analyses.

Nuclear magnetic resonance spectroscopy (NMR) analysis of bio-oil was conducted for determining the functional group distribution in bio-oil. The solution-state (acetone-d_6) ^{13}C NMR spectra of whole bio-oil were recorded on an NMR spectrometer (AV-600, Bruker, Germany) at 30 °C using a 5 mm broad band probe. About 10^4 scans were accumulated for each ^{13}C spectrum with a sweep width of 30,000 Hz and a 90° pluse angle. Inverse gated decoupling was applied to void NOE effects, and a 6 s relaxation delay was used between scans, which allows for accurate integration of ^{13}C signals.

Physical properties of bio-oil including water content, kinematic viscosity, pH, and calorific value were analyzed. The water content of bio-oil was measured by Karl Fischer titrimetry (787KF Titrino, Metrohm, Switzerland) using ASTM Method D-1744. The kinematic viscosity was determined with a kinematic viscometer (WYF108, Wuzhou, Dalian) at 40 °C. The calorific value was determined as higher heating value (HHV) by an isoperibol oxygen bomb calorimeter (WZR-IT-C, BTYQ, Changsha). The pH was directly analyzed by a pH meter (PHS-3C, SPSIC, Shanghai). Three parallel tests were performed for each analysis. The reported results were the average of three tests.

3. Results and discussion

3.1. Chemical component analysis of pretreated eucalyptus wood

The pretreated eucalyptus wood obtained from hydrothermal pretreatment at 160, 170, 180 and 190 °C are respectively named PE-160, PE-170, PE-180, and PE-190. The mass yield and chemical component analysis results of pretreated eucalyptus wood are presented in Table 1. The mass yield of pretreated eucalyptus wood decreases with the increasing pretreatment temperature from 96.45% at 160 °C to 73.29% at 190 °C owing to the decomposition of main chemical components in eucalyptus wood. The hemicellulose content in pretreated eucalyptus wood is evidently lower than that in original eucalyptus wood and significantly decreases with the increasing pretreatment temperature from 21.85% in PE-160 to 3.47% in PE-190. Among all chemical components in eucalyptus wood, the hemicellulose shows the highest degree of decomposition during hydrothermal pretreatment as shown by the low recovery rate of hemicellulose in pretreated eucalyptus wood, which confirms the fact that most hemicellulose in biomass can be decomposed during hydrothermal pretreatment. Although part of cellulose is also decomposed during hydrothermal pretreatment as shown by the decreased recovery rate of cellulose, the cellulose content in pretreated eucalyptus wood is conversely increased as a

Table 2
The effect of hydrothermal pretreatment on metal content in eucalyptus wood (on dry basis).

Metals	Content of metals (ppm)				
	Eucalyptus wood	PE-160	PE-170	PE-180	PE-190
Na	38.5	19.7	20.9	16.2	15.4
K	538.4	33.6	36.8	26.5	24.2
Mg	175.6	146.9	117.6	80.4	57.7
Ca	707.6	1244.6	976.5	729.9	505.1
Al	35.9	20.6	22.6	22.3	18.7
Fe	174.6	92.0	130.8	88.9	101.3
Mn	86.2	35.5	20.2	5.8	4.8
Cu	1.3	1.0	1.3	2.3	2.3

result of the decomposition of hemicellulose. In previous studies about biomass torrefaction, most hemicellulose could also be removed from biomass. Nevertheless, the content of acid insoluble fibers in torrefied biomass were apparently enhanced and more acid insoluble fibers were formed through the charring and cross-linking of cellulose and lignin in biomass, which had a negative impact on the fast pyrlysis of torrefied biomass and contributed to the significant bio-oil yield penalties (Chang et al., 2012; Phanphanich and Mani, 2011). However, during hydrothermal pretreatment of eucalyptus wood, the acid insoluble fibers in pretreated eucalyptus wood show relatively less content variation and the recovery rate of acid insoluble fibers is reduced as show in Table 1, which suggests that the charring and cross-linking of cellulose and lignin can be avoided and the formation of more acid insoluble fibers is inhibited in hydrothermal pretreatment of eucalyptus wood. Compared to torrefaction, hydrothermal pretreatment may be more effective method for selectively removing the hemicellulose from biomass.

3.2. Metal analysis of pretreated eucalyptus wood

The effect of hydrothermal pretreatment on the metal content in eucalyptus wood is presented in Table 2. Some metals consisting of Na, K, Mg, Al, Fe, and Mn in pretreated eucalyptus wood exhibit relatively lower content that in original eucalyptus wood. This indicates that part of metals can be solubilized in hot compressed water and removed from eucalyptus wood during the hydrothermal pretreatment. However, the content of Ca in pretreated eucalyptus wood obtained at 160, 170, and 180 °C is enhanced as can be seen in Table 2, which suggests that Ca may be resistive to hydrothermal pretreatment. The different metals may present the individual existing form in biomass and some metals can be bound to biomass polymers by associating with the oxygen-containing functional groups in polymers such as hydroxyl groups in cellulose or lignin (Mayer et al., 2012). This results in the solubility diversity of different metals in hot compressed water. Small amount of inorganic mineral matters in biomass can dramatically alter the pyrlosis speciation and product properties through the catalytic cracking reaction in fast pyrolysis (Raveendran et al., 1995). Therefore, the variation in metals contents will influence the product distribution and properties of bio-oil from fast pyrolysis of pretreated eucalyptus wood.

3.3. Products distribution of fast prolysis

Three-phase products distribution in fast pyrolysis of original and pretreated eucalyptus wood is depicted in Fig. 3. Hydrothermal pretreatment exerts a great effect on the products distribution in fast pyrolysis of eucalyptus wood. The pretreated eucalyptus wood gives higher bio-oil yield and lower char and gas yields in fast pyrolysis than original eucalyptus wood, and the bio-oil yield based on pretreated eucalyptus wood increases with the elevated pretreatment temperature as shown in Fig. 3. The changes of chemical composition involving organic polymers and inorganic salts in pretreated eucalyptus wood are responsible for the variation in pyrolysis products distribution. In previous studies about fast pyrolysis of torrefied biomass, the torrefied biomass usually give lower bio-oil yield and higher char yields than original biomass, which is ascribed to charring and cross-linking of biomass constituents during torrefaction (Zheng et al., 2012, 2013). However, in the present study chemical components in eucalyptus wood do not appear to suffer from the severe charring and cross-linking during hydrothermal pretreatment, and cellulose content in pretreated eucalyptus wood apparently increases due to the significant degradation of hemicellulose as mentioned in chemical component analysis. Thus the bio-oil yield in fast pyrolysis of pretreated eucalyptus wood is not lowered instead of being enhanced. In addition, the decrease of some metals contents in pretreated eucalyptus wood may also help to restrain the formation of gas products and char and improve the bio-oil yield in fast pyrolysis by reducing catalytic cracking reaction.

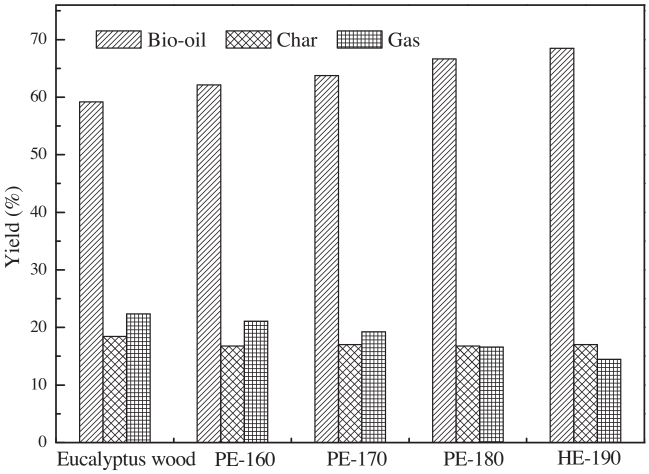

Fig. 3. Three-phase products distribution in fast pyrolysis of original and pretreated eucalyptus wood.

However, bio-oil yields based on original eucalyptus wood are lowered after eucalyptus wood is partly degraded during hydrothermal treatment. Actually, fast pyrolysis aided by hydrothermal pretreatment can be considered a step-wise conversion process, where some high value chemicals from hydrothermal pretreatment and bio-oil from fast pyrolysis can be obtained. The optimum pretreatment condition can only be determined after considering yields and properties of two-staged liquid products.

3.4. GC/MS analysis of bio-oil

The bio-oils from fast pyrolysis of original and pretreated eucalyptus wood obtained at 160, 170, 180, and 190 °C are respectively named BE, BPE-160, BPE-170, BPE-180, and BPE-190. The chemical composition of bio-oil is first examined by GC/MS analysis, and the quantitative results of main compounds in bio-oil are listed in Table 3. It can be seen from Table 3 that main compounds in bio-oil detected by GC/MS are composed of ketones, aldehydes, organic acids, furans, phenols, and levoglucosan. Owing to the modified chemical composition during hydrothermal treatment, there is an evident change in compounds distribution profile of BPE. Hydroxyacetone, 1,2-cyclopentanedione, and 3-methyl-1,2-cyclopentanedione make up the main ketone products, while 2-butenal is the only detected aldehyde product. The contents of nearly all ketone

Table 3
Quantitative analysis of main compounds in bio-oils from fast pyrolysis of original and pretreated eucalyptus wood.

Time (min)	Compounds	Content of compounds in bio-oil (wt%)				
		BE	BPE-160	BPE-170	BPE-180	BPE-190
3.24	2,3-Butanedione	0.16	0.12	0.13	0.09	0.08
3.99	2-Butenal	0.15	0.13	0.13	0.09	0.06
5.15	(E)-3-penten-2-one	0.05	0.03	0.03	0.02	0.01
8.06	Hydroxyacetone	1.96	1.43	1.23	1.13	1.05
9.05	2-Cyclopenten-1-one	0.14	0.08	0.08	0.06	0.05
9.27	2-Methyl-2-cyclopenten-1-one	0.06	0.04	0.03	0.02	0.02
9.47	1-Hydroxy-2-butanone	0.18	0.11	0.10	0.09	0.11
12.57	3-Methyl-2-cyclopenten-1-one	0.06	0.03	0.03	0.03	0.02
14.30	4-Cyclopentene-1,3-dione	0.02	0.02	0.02	0.02	0.01
17.91	1,2-Cyclopentanedione	0.35	0.21	0.25	0.21	0.20
18.83	3-Methyl-1,2-Cyclopentanedione	0.25	0.13	0.14	0.12	0.13
19.80	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.03	0.01	0.01	0.01	0.01
Total of ketones and aldehydes		3.41	2.34	2.18	1.89	1.75
11.33	Acetic acid	4.65	4.13	3.93	2.28	1.59
13.43	Propanoic acid	0.10	0.09	0.16	0.16	0.16
15.44	Butanoic acid	0.06	0.06	0.05	0.03	0.03
Total of acids		4.81	4.28	4.14	2.47	1.78
11.43	Furfural	0.63	0.56	0.55	0.44	0.38
13.98	5-Methylfurfural	0.06	0.06	0.06	0.06	0.10
15.92	2-Furanmethanol	0.09	0.07	0.06	0.07	0.08
16.22	5-Methyl-2(5H)-furanone	0.05	0.04	0.04	0.03	0.03
16.94	3-Methyl-2(5H)-furanone	0.04	0.03	0.04	0.03	0.03
17.64	2(5H)-furanone	0.12	0.08	0.10	0.09	0.08
19.75	4-Methyl-5H-furan-2-one	0.05	0.04	0.05	0.05	0.04
27.17	5-Hydrxoymethylfurfural	0.15	0.30	0.35	0.44	0.54
Totals of furans		1.19	1.18	1.25	1.21	1.28
19.32	Guaiacol	0.19	0.13	0.16	0.18	0.20
20.70	4-Methylguaiacol	0.13	0.14	0.17	0.19	0.21
21.40	*o*-Cresol	0.05	0.02	0.03	0.03	0.02
21.45	Phenol	0.08	0.05	0.05	0.04	0.04
21.69	4-Ethylguaiacol	0.06	0.05	0.06	0.06	0.06
22.42	*p*-Cresol	0.03	0.02	0.02	0.02	0.02
22.52	*m*-Cresol	0.06	0.04	0.04	0.03	0.03
23.41	Eugenol	0.07	0.05	0.06	0.06	0.05
23.77	4-Vinylguaiacol	0.15	0.13	0.15	0.15	0.14
24.45	Isoeugenol	0.04	0.03	0.03	0.02	0.03
24.55	Syringol	0.48	0.27	0.32	0.38	0.44
25.49	4-Hydroxy-3-methoxybenzoic acid	0.55	0.54	0.63	0.69	0.76
26.11	2′,6′-Dihydroxy-4′-methoxyacetophenone	0.14	0.11	0.13	0.13	0.16
27.86	Vanillin	0.44	0.34	0.41	0.42	0.39
28.26	4-Propylguaiacol	0.04	0.05	0.06	0.06	0.05
28.70	Acetovanillone	0.06	0.05	0.06	0.06	0.05
28.92	Homovanillic acid	0.04	0.03	0.03	0.03	0.04
29.86	4-Allylsyringol	0.75	0.67	0.83	0.94	0.90
33.84	Syringaldehyde	0.25	0.26	0.33	0.35	0.33
35.05	Acetosyringone	0.14	0.13	0.16	0.19	0.19
39.72	4-Hydroxy-2-methoxycinnamaldehyde	0.07	0.06	0.06	0.06	0.05
Totals of phenols		3.82	3.17	3.79	4.09	4.16
49.75	Levoglucosan	4.13	10.83	11.90	15.36	18.00

and aldehyde products in bio-oil are reduced through hydrothermal pretreatment as shown in Table 3. This can be partly explained by the removal of hemicellulose from eucalyptus wood. The reduction in the content of aldehydes and ketones will enhance the thermal stability of bio-oil. Acetic acid is the major organic acid with the content of 4.65% in BE and mainly derived from the elimination reaction of acetyl groups in hemicellulose structure. The content of acetyl groups in pretreated eucalyptus wood can be reduced as hemicellulose is removed. As a result, the content of acetic acid in BPE is lower than that in BE and apparently decreases as pretreatment temperature rises from 4.13% for BPE-160 to 1.59% for BPE-190 as can be seen in Table 3. The decease of acetic acid content probably reduces the corrosion of bio-oil. Furfural and 5-hydroxymethylfurfural (5-MHF) are the major furan products. It is found from Table 3 that the content of furfural is reduced in BPE, which can be also attributed to the removal of hemicellulose during hydrothermal treatment, while the content of 5-MHF that is mainly originated from cellulose pyrolysis is inversely enhanced, which indicates hydrothermal treatment favors the formation of 5-MHF. A considerable amount of levoglucosan (LG) is detected by GC/MS, which is the typical cellulose-derived pyrolysis product and is utilized in the synthesis of various chemicals. LG content in BE reaches 4.13%, while the LG content in BPE dramatically increases with the elevated pretreatment temperature from 10.83% for BPE-160 to 18.00% for BPE-190, which reveals that hydrothermal pretreatment significantly promotes the formation of LG. The content variation of cellulose-derived pyrolysis product in bio-oil may be indicative of the change of cellulose pyrolysis mechanism. A series of prarallel or sequential reactions that take place in cellulose pyrolysis account for the formation of main products (Patwardhan et al., 2009; Piskorz et al., 1989). LG is originated from the cleavage of the glycosidic linkage in cellulose and subsequent intramolecular rearrangement of the formed monomer units. 5-MHF as a ring-containing product is generally involved in the

Table 4
^{13}C NMR integrations of bio-oils from fast pyrolysis of original and pretreated eucalyptus wood.

Chemical shift region (ppm)	Carbon assignments	Carbon content (%)				
		BE	BPE-160	BPE-170	BPE-180	BPE-190
0–28	Short aliphatics	13.1	11.4	8.9	9.0	8.9
28–55	Long and branched aliphatics	6.3	4.4	4.9	1.3	1.3
0–55	All of alkyl carbons above	19.4	15.8	13.8	10.3	10.2
55–95	Alcohols, ethers, methoxyl, carbonhydrates	26.6	37.8	38.0	42.4	41.5
95–165	Aromatics	43.8	38.5	41.3	43.9	45.2
165–180	Carboxylic acids, esters	6.0	4.3	3.6	1.7	1.4
180–215	Aldehydes, ketones	4.2	3.6	3.3	1.7	1.7
165–215	All of carbonyl carbons above	10.2	7.9	6.9	3.4	3.1

ring-opening and rearrangement reaction (Shen et al., 2010). The ring fragmentation of cellulose itself or the formed LG will form some lightweight compounds such as ketones and aldehydes (Piskorz et al., 1989). The catalysis of mineral matters and the interaction of organic polymers determine the reaction pathway above. Especially, small amount of inorganic salts containing alkali or alkaline earth cations can retard the formation of LG through suppressing the unzipping reaction at the free chain ends of cellulose. Meanwhile, the ring scission of cellulose can be promoted by direct catalysis of inorganic salts. In previous studies, it was found that K^+ and Na^+ demonstrated the most remarkable influence on the cellulose pyrolysis (Patwardhan et al., 2010; Yang et al., 2006). The significant removal of K and Na during hydrothermal pretreatment can be achieved as can be seen in the metal analysis of eucalyptus wood above, which promotes the formation of LG in fast pyrolysis of pretreated eucalyptus wood and reduces the formation of lightweight compounds. Thus bio-oils from fast pyrolysis of pretreated eucalyptus wood reveal much higher LG content. A considerable number of phenols are also detected by GC/MS. The total contents of phenols in BPE-160 and BPE-170 are lower than that in BE as shown in Table 3, which can be explained by the removal of some thermally unstable lignin units from eucalyptus wood during hydrothermal treatment. However, the total phenols contents are enhanced in BPE-180 and BPE-190. This may be attributed to the increase of lignin contents in PE-180 and PE-190.

3.5. ^{13}C NMR analysis of bio-oil

Only part of compounds in boil-oil can be analyzed by GC, while an overall insight into the nearly entire bio-oil rather than a fraction of it may be gained by NMR analysis. The integrated ^{13}C spectra of bio-oil are summarized in Table 4. The information on the types of chemical functional groups within a given chemical shift region and their corresponding content in entire carbons can be obtained in Table 4. Hydrothermal pretreatment results in the change of overall functional groups distribution in BPE. Alkyl carbons are found in the range of 0–55 ppm, which are further subdivided into short aliphatic carbons in the range of 0–28 ppm and long and branched aliphatic carbons in the range of 28–55 ppm (Mullen et al., 2009). The BPE exhibits lower alkyl carbons contents than BE as shown in Table 4. The carbons found in range of 55–95 ppm may be contained in alcohols, ethers, methoxyl, and carbonhydrates. The BPE shows much higher carbons content in this region than BE, which can be explained by the increase of LG content in bio-oil as analyzed in GC/MS. Aromatic carbons existing in the form of lightweight phenols and lignin oligomers are found in the range of 95–165 ppm. Aromatic carbon content in BPE-160 and BPE-170 is reduced, while it is enhanced in BPE-190. Acid and ester carbonyl carbons are found in the range of 165–180 ppm, while aldehyde and ketone carbonyl carbons are found above 180 ppm. The carbonyl carbons in BPE are lower than that in BE and decrease with the increasing pretreatment temperature, which will help to enhance the thermal stability of BPE, and the result is the same as that from GC/MS analysis.

Table 5
Physical properties analyses of bio-oils from fast pyrolysis of original and pretreated eucalyptus wood.

Physical properties	BE	BPE-160	BPE-170	BPE-180	BPE-190
Water content (wt%)	26	21	19	18	18
Kinematic viscosity (cSt)	15.1	27.0	39.9	64.1	72.3
HHV (MJ/kg)	16.62	17.68	17.91	18.35	18.42
pH	3.13	3.15	3.14	3.17	3.15

In conclusion, hydrothermal pretreatment can improve chemical composition of bio-oil, and significantly promote the formation of levoglucosan in fast pyrolysis of pretreated eucalyptus wood. Although the high-cost drying process is required before fast pyrolysis of hydrothermally pretreated biomass, the step-wise conversion of biomass constituents can be achieved by the combination of hydrothermal pretreatment and fast pyrolysis, where step-wise products consisting of liquid product from hydrothermal pretreatment and bio-oil from fast pyrolysis can be acquired, and the economy of step-wise conversion process may be improved owing to increased yields of step-wise target chemicals. In further studies, two-staged liquid products from hydrothermal pretreatment and fast pyrolysis will be investigated. In addition, hydrothermally pretreated biomass will be subjected to the microwave-induce pyrolysis to obtain levoglucosan-rich liquid product, where the drying process of pretreated biomass will be not needed.

3.6. Physical properties of bio-oil

Physical properties of bio-oils from fast pyrolysis of original and pretreated eucalyptus wood are summarized in Table 5. The water content in BE reaches 26%, while water content in BPE is evidently lower and decreases with the elevated pretreatment temperature from 21% for BPE-160 to 18% for BPE-180 and BPE-190 as can be seen in Table 5. This suggests that the dehydration reaction is significantly reduced in the fast pyrolysis of pretreated eucalyptus wood owing to the removal of hemicellulose and the variation in the cellulose pyrolysis mechanism. The reduction of water content contributes to the increase in higher heating value of BPE. Therefore, Hydrothermal pretreatment has the positive impact on the fuel properties of bio-oil. However, the kinematic viscosity of BPE is enhanced due to the decrease in contents of water and lightweight compounds in BPE, which could be unfavorable to the bio-oil application in thermal devices. The pH of bio-oil depends on the chemical composition of bio-oil, but the variation in chemical composition of BPE do not result in the evident pH changes as shown in Table 5.

4. Conclusions

Chemical composition of eucalyptus wood was modified by hydrothermal pretreatment. Hemicellulose and some metals were effectively removed from eucalyptus wood, while cellulose content was enhanced. No significant charring and carbonization of constituents was observed during hydrothermal pretreatment. The pretreated eucalyptus wood gave higher bio-oil yield that original eucalyptus wood. The contents of ketones and acids in bio-oils produced from pretreated eucalyptus wood were reduced, while levoglucosan content was dramatically enhanced. The water content in bio-oils produced from pretreated eucalyptus wood was lowered, which contributed to improved heating value. Therefore, higher quality bio-oil could be obtained by hydrothermal pretreatment.

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